Synthesis, Characterization, and Catalytic Activity of 4 mol % N,N'-Methylene Bisacrylamide Crosslinked Poly(acrylic acid)–Metal Complexes

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ABSTRACT: The metal-ion complexation behavior and catalytic activity of 4 mol % N,N'-methylene bisacrylamide crosslinked poly(acrylic acid) were investigated. The polymeric ligand was prepared by solution polymerization. The metal-ion complexation was studied with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal uptake followed the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II). The polymeric ligand and the metal complexes were characterized by various spectral methods. The catalytic activity of the metal complexes were investigated toward the hydrolysis of p-nitrophenyl acetate (NPA). The Co(II) complexes exhibited high catalytic activity. The kinetics of catalysis was first order. The hydrolysis was controlled by pH, time, amount of catalyst, and temperature. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 272–279, 2004

Key words: catalysts; metal-polymer complexes; swelling

INTRODUCTION

Polymer–metal complexes are currently attracting considerable attention for a variety of applications, including development in nuclear chemistry, organic synthesis, wastewater treatment, pollution control, hydrometallurgy, polymer drug grafts, preconcentration, recovery of trace metal ions, and catalysts.[1–6] In macromolecular metal complexes, the physicochemical properties and chemical reactivities of the complex moieties are often strongly affected by interaction with the surrounding three-dimensional polymer matrix. The nature of the polymer backbone, the conformation of the macromolecular chain, the microenvironment of the reactive functional groups, the relative occurrence of functional groups in the polymer chain, the stereochemistry around the functional groups, the overall topology of the macromolecular matrix, and the solvation and swelling characteristics determine the reactivity of a functional group attached to a macromolecular backbone. A polymer–metal complex is composed of a synthetic polymer and a metal ion. Its synthesis represents an attempt to give an organic polymer inorganic functions. Polymer–metal complexes show unique properties that are distinctly different from those of their low-molecular-weight analogues. This has led to fundamental research on the heterogeneous environment provided by polymers.[7]

Polymer–metal complexes are markedly useful as immobilized catalysts for practical use because they are more reactive than the corresponding monomeric analogue because of the specificity induced by the macromolecular matrix. In addition to catalytic activity, they have immense application in various areas such as conductivity,[8,9] the modification of material surfaces by the binding of metal complexes,[10,11] the separation of metal ions,[12–14] and the mimicking of bioinorganic systems.[15,16] Geckeler studied the applications of polymer–metal complexes for environmental protection.[17] Kargoz discussed the preparation of a modified polyacrylamide hydrogel and its application in the removal of Cu(II) ion.[18]

This study dealt with the synthesis and characterization of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes of 4 mol % N,N'-methylene bisacrylamide (NNMBA)-crosslinked poly(acrylic acid) (PAA) and the catalytic activity of these complexes in the hydrolysis of an active ester, p-nitrophenyl acetate (NPA).

EXPERIMENTAL

Materials and methods

The polymer used in this investigation was synthesized in the laboratory. NNMBA was purchased from Aldrich Chemical Co. (Milwaukee, WI). Acrylic acid was obtained from Fluka (Switzerland). p-Nitrophenyl acetate was purchased from SRL (Mumbai, India). All metal salts were commercially available. All of the solvents and reagents were purified by literature procedures.

Physicochemical measurements

Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS-55 spectrometer with KBr pellets. Ultraviolet–visible (UV–vis) spectra were recorded on a Shimadzu UV-160A spectrophotometer. The cross-polarity/magic-angle spinning (CP-MAS) ^{13}C-NMR spectrum was recorded with a DSX 300 MHz instrument. A Shimadzu D-740 thermal analyzer at a heating rate of 10°C min^{-1} was used to evaluate the thermal stability of the complexes. The electron paramagnetic resonance (EPR) spectrum was recorded on a Varian E-4X band spectrophotometer at 303 K under a nitrogen atmosphere. Scanning electron microscopy (SEM) was done with a Jeol JSM 35 CF model.

Preparation of 4 mol % NNMBA-crosslinked PAA

For the preparation of 4 mol % NNMBA-crosslinked PAA, water (60 mL) and azobisisobutyronitrile (AIBN; 0.5 g) were heated in an oil bath with stirring. When the temperature was 85–90°C, a mixture of acrylic acid (6.59 mL) and NNMBA (0.62 g) was added to water containing AIBN. Stirring was continued with the temperature kept constant until a glassy solid mass separated out. Polymerization was carried out under a nitrogen atmosphere. The polymer was collected and washed with distilled water and Soxhlet extracted with acetone and dried *in vacuo* (yield = 6.5 g). The polymer was characterized by FTIR and ^{13}C-NMR CP-MAS spectra.[19]

Preparation of the sodium salt of NNMBA-crosslinked PAA

Because of the complexing difficulty of the carboxyl group of the PAA, we converted NNMBA-crosslinked PAA to its sodium salt. Derivatization was effected at the carboxyl group of the acrylic acid unit. For this, the polymer was treated with excess sodium hydroxide solution (0.2*M*) with stirring for 24 h. The resin complex was filtered and washed with distilled water until the filtrate was free from excess NaOH.

Estimation of the carboxyl capacity of the sodium salt of NNMBA-crosslinked PAA

For the determination of carboxyl capacity, the sodium salt of NNMBA-crosslinked PAA (100 mg) was equilibrated with HCl (0.2*N*, 10 mL) for 24 h with stirring. The resin sample was filtered and washed with distilled water to remove unreacted HCl; the filtrate was titrated against NaOH (0.2*N*) to a phenolphthalein end point. The carboxyl capacity of the polymer was 8.96 mmol/g.

Preparation of polymer–metal complexes

Polymeric ligand (100 mg) was stirred with 50 mL (0.05*M*) of a metal salt solution for about 8 h at its natural pH. The metal salts used were chromium chloride, manganese chloride, ferric chloride, cobaltous chloride, nickel sulfate, and copper sulfate. The polymer–metal complexes were washed with distilled water to remove the uncomplexed metal ions. From the decrease in the concentration of the metal-ion solution, the amount of metal ion complexed by 100 mg of polymer was calculated. The metal complexes were dried *in vacuo*. The concentrations of Cr(III), Fe(III), Co(II), Ni(II), and Cu(II) solutions were determined by spectrophotometric methods, and those of Zn(II) and Mn(II) were calculated by standard titrimetric methods.[20] The metal uptake decreased in the order Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II).

Influence of pH on metal-ion binding

The metal-ion uptake of the resin was studied at different pH to get the optimum pH for maximum complexation. The pH of the metal solution was adjusted by the addition of 1*M* hydrochloric acid or 1*M* NaOH as shown by a pH meter. To different sets of polymeric ligands (50 mg), metal salt solutions at different pH values were added and stirred. At 0.05*M*, the natural pH values for the different metal ions were Cr(III) = 2.6, Mn(II) = 4.41, Fe(III) = 2.2, Co(II) = 5.8, Ni(II) = 5.1, Cu(II) = 4.46, and Zn(II) = 5.34. The metal-ion binding studies were carried out in a thermostated shaker for 8 h. The metal uptake was followed as mentioned previously.

Swelling studies

A certain amount (200 mg) each of the PAA, its sodium salt, and Cu(II) complex were equilibrated with 50 mL of distilled water for 48 h. The excess water was removed carefully by centrifuging, and the swollen weights were determined. The samples were dried *in vacuo* for 24 h, and finally, the weight of the dry resins were also determined. From the weights of the wet and dry resins, the equilibrium water content (EWC) was calculated by the expression

$$EWC(\%)$$

$$= \frac{\text{Weight of wet resin} - \text{Weight of dry resin}}{\text{Weight of wet resin}}$$

$$\times 100$$

Catalytic activity of 4 mol % NNMBA-crosslinked PAA–metal complexes in the hydrolysis of *p*-nitrophenyl acetate: General procedure

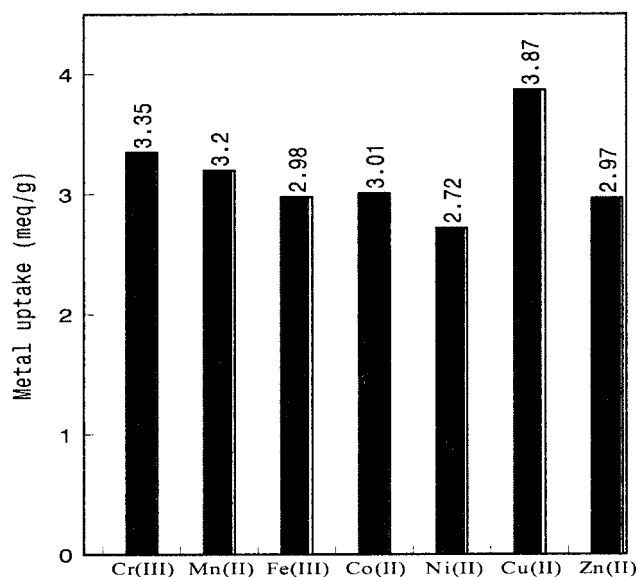*p*-Nitrophenyl acetate was dissolved in dioxane (2 mL), and phosphate buffer (0.05*M*, 48 mL) of a definite pH

Figure 1 Metal uptake of the sodium salt of 4 mol % NNMBA-crosslinked PAA.

was added. A weighed quantity (4×10^{-4} M metal centers) of the polymer–metal complex was added to the previous solution at room temperature, and the mixture was stirred. The concentration of p-nitrophenol liberated at different time intervals was measured from the absorbance at 400 nm. A blank was run with the ester in dioxane–buffer without the metal complex. The effect of various parameters such as temperature, amount of catalyst, pH, and concentration of buffer were also followed.

RESULTS AND DISCUSSION

Preparation of polymer–metal complexes

The complexation behavior of ligand functions supported on a polymer is generally different from the corresponding low-molecular-weight analogue.[21–23] This variation is connected with the polymer matrix to which the ligand function is attached.

The complexation of the sodium salt of 4 mol % NNMBA-crosslinked PAA was investigated for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions (0.05M) at their natural pH by the batch equilibration method. In all of the complexation experiments, to a definite amount of the polymeric ligand, a known concentration of excess metal salt solution was added and stirred. The decrease in the concentration of the metal-ion solution was determined spectrophotometrically or titrimetrically. In this study, the metal uptake decreased in the order Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II) (Fig. 1).

Influence of pH on the metal-ion complexation

The metal-ion complexation of a polymeric ligand is highly dependent on the equilibrium pH of the medi-

um.[24,25] The pH dependence of metal-ion complexation was used for the selective separation of metal ions from a mixture of metal ions. In this study, because most of the metal ions were prone to precipitation at higher pH values, investigations were limited up to those pH values where precipitation was just prevented. The use of a buffer solution for adjusting the pH was avoided because of the undesirable results from the coordination of the ionic species with metal ions.[26] The effect of pH on the complexation of metal ions with 4 mol % NNMBA-crosslinked PAA is depicted in Figure 2.

Swelling studies

For a crosslinked polymer, the extent of swelling depends on the solvent–polymer interaction, which is determined not only by the nature of the solvent and the polymer matrix but also by the active groups introduced into the polymer matrix. The presence of hydrophobic/hydrophilic crosslinking agents lead to the formation of crosslinked systems with varying solvation and swelling characteristics.

The EWCs of 4% NNMBA-crosslinked PAA, the sodium salt of PAA, and its Cu(II) complex were carried out in distilled water, and the results are shown in Figure 3. The swelling of the sodium salt was higher than that of the respective crosslinked PAA. In the metal-ion complexed state, the ligand groups were less amenable for binding with water, and hence, the EWC values decreased. The complexation with metal ions acted as additional crosslinking, resulting in decreased swelling.
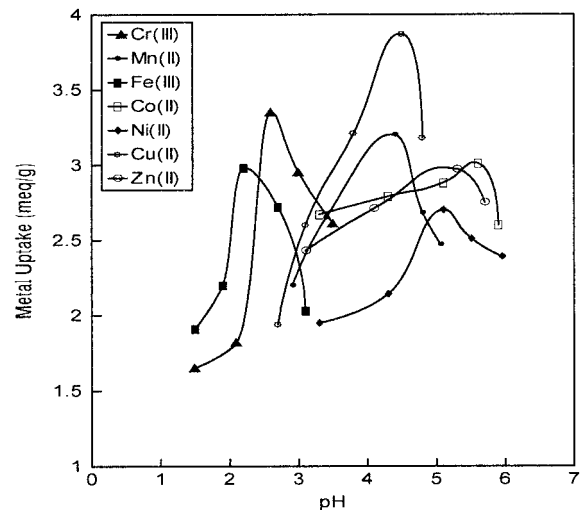

Figure 2 Effect of pH on the metal-ion complexation of the sodium salt of 4 mol % NNMBA-crosslinked PAA.
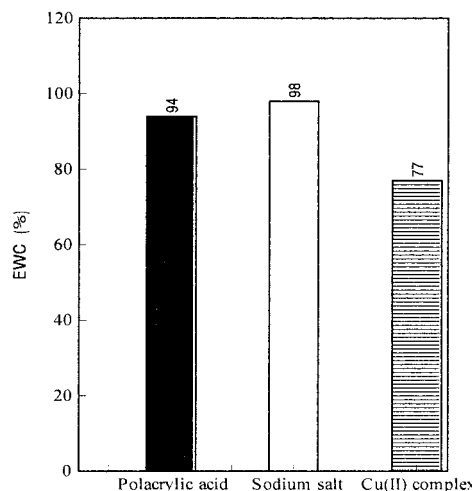
Figure 3 Swelling characteristics of the sodium salt of 4 mol % NNMBA-crosslinked PAA and its Cu(II) complex.

Characterization of 4 mol % NNMBA-crosslinked PAA and metal complexes

FTIR spectra

The FTIR spectra of 4 mol % NNMBA-crosslinked PAA and its Cu(II) complex had a very broad intense band at 3300–3500-cm^{-1} region because of the O—H stretching of the carboxyl group. The weaker C—H stretching bands were seen superimposed upon the broad O—H band. A fine structure was observed on the long wavelength side of the broad O—H band represented overtones and a combination tones of fundamental bands occurring at the long wavelength. The >C=O group in 4 mol % NNMBA-crosslinked PAA showed an absorbance at 1728 cm^{-1} with a small shoulder at 1703 cm^{-1}. Complexation with the Cu(II) ion resulted in the shift of absorption from 1728 to 1694 cm^{-1} and 1703 to 1663 cm^{-1}. The O—H bending appeared at 1460 cm^{-1} in the FTIR spectrum of 4 mol % NNMBA-crosslinked PAA and shifted to 1406 cm^{-1} in the case of the Cu(II) complex. This was because of the complexation through the carboxyl group.

The absorption at 1660 cm^{-1} in the FTIR spectra of 4 mol % NNMBA-crosslinked PAA was due to the >N—H stretching of the secondary amide of the NNMBA crosslinking agent.

^{13}C-NMR CP-MAS spectrum

The ^{13}C-NMR CP-MAS spectrum of 4 mol % NNMBA-crosslinked PAA is shown in Figure 4. The backbone methylene carbon appeared as a very sharp peak at 43.902 ppm. An intense peak at 180.556 ppm was due to the >C=O of the carboxylate group.

UV–vis spectra

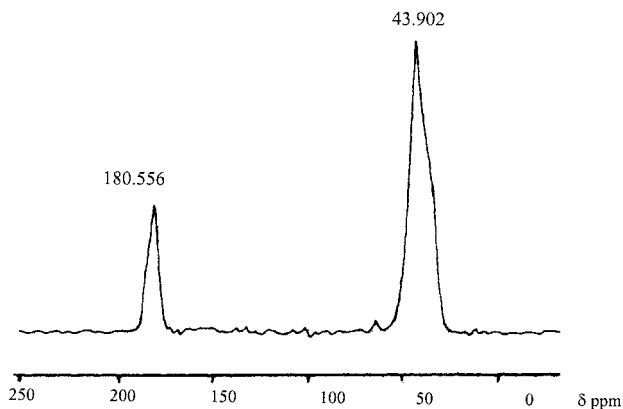UV–vis spectra provide an accurate and simple method for the determination of the geometry of poly-

Figure 4 ^{13}C-NMR CP-MAS spectrum of 4 mol % NNMBA-crosslinked PAA.

mer–metal complexes.[27] The structure and geometry of polymer–metal complexes are determined by the microenvironment of the polymer domain. The actual position of the band maxima observed in the electronic spectra is a function of the geometry and the strength of the coordinating ligand.

The typical transitions of the Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes of 4 mol % NNMBA-crosslinked PAA are given in Table I.

Two bands corresponding to $^4A_{2g}$–$^4T_{2g}$ (17,391–17,761 cm^{-1}) and $^4A_{2g}$–$^4T_{1g}$ (F; 23,640–23,809 cm^{-1}) transitions were observed in the UV–vis spectra of the Cr(III) complexes. These transitions led to an octahedral geometry for the Cr(III) complexes. In Mn(II), there are five unpaired electrons with parallel spins. Any electronic transition within the d level must involve a reversal of spins; hence, adsorption bands will be extremely weak. This accounted for the pale pink color of the Mn(II) complexes. Mn(II) complexes gave a broad band corresponding to the combined transitions $^6A_{1g}$–^4Eg and $^6A_{1g}$–$^4A_{1g}$ with an octahedral geometry. Fe(III) also had a d^5 electronic configuration with five unpaired electrons in a high-spin octahedral field. In this study, the Fe(III) complexes exhibited two bands corresponding to $^6A_{1g}$–$^4T_{1g}$ and $^6A_{1g}$–$^4T_{2g}$

TABLE I
Details of the Electronic Spectra of 4 mol% NNMBA-Crosslinked PAA-Metal Complexes

Metal complex	Band assigned (cm^{-1})	Type of transition
Cr(III)	17,006	$^4A_{2g}$–$^4T_{2g}$
	23,752	$^4A_{2g}$–$^4T_{1g}$ (F)
Mn(II)	21,834	$^6A_{1g}$–$^4E_g{}^4A_{1g}$
Fe(III)	15,576	$^6A_{1g}$–$^4T_{1g}$
	21,276	$^6A_{1g}$–$^4T_{2g}$
Co(II)	17,638	$^4T_{1g}$–$^4T_{2g}$
	32,894	$^4T_{1g}$–$^4T_{1g}$ (P)
Ni(II)	24,814	$^3A_{2g}$–$^3T_{1g}$ (P)
	13,280	$^3A_{2g}$–$^3T_{1g}$ (F)
Cu(II)	14,576	$^2E_{2g}$–$^2T_{2g}$

Figure 5 EPR spectrum of the Cu(II) complex of the sodium salt of 4 mol % NNMBA-crosslinked PAA.

transitions. Fe(III) had an extra charge compared to Mn(II); hence, it was more able to polarize the ligands, and hence, there was a chance for charge-transfer spectra. Fe(III) complexes were more colored than Mn(II) complexes. Co(II) complexes were tetrahedral or octahedral. The tetrahedral complexes of Co(II) were intensely blue compared with the pale pink color of the octahedral complexes. The deep blue color of the Co(II) complexes of this study changed to pink when they were exposed to moisture because of the change in geometry. The UV–vis spectra of the Ni(II) complexes of NNMBA-crosslinked PAA gave two spin-allowed transitions: ^3A_2g–^3T_1g (F; 18,518–18,867 cm^{-1}) and ^3A_2g–^3T_1g (P; 24,390–24,875 cm^{-1}) in an octahedral field. In the Cu(II) complex, the broad absorption band in the region 13,947–14,084 cm^{-1} was due to ^2Eg–^2T_2g transition in a distorted octahedral field[28] (Jahn–Teller effect). So there was more than one transition. This overlap resulted in an asymmetrical broad band. In the polymer-anchored Zn(II) complex, the spectrum obtained was ligand related, and no d–d transition occurred. Therefore, it would have had a tetrahedral geometry.

EPR spectrum

The EPR spectrum of the 4 mol % NNMBA-crosslinked PAA Cu(II) complex at liquid nitrogen temperature is shown in Figure 5.

The EPR parameters gave a measure of the nature of the complexation with the metal ion. The EPR parameters calculated for the copper complex were $g_\parallel = 2.32$, $g_\perp = 2.05$, $A_\parallel = 140$, $A_\perp = 96.66$, $\alpha^2Cu = 0.7599$, and $g_{av} = 2.14$.

The values of $g_\parallel > g_\perp$ showed that the unpaired electron was in the $dx^2 - y^2$ orbital of the Cu(II) ion and had spectral characteristics of axial symmetry. The bonding parameter (α^2Cu) was calculated by the expression given by Kivelson and Neiman:[29]

$$\alpha^2Cu = -(A_\parallel/0.036) + (g_\parallel - 2.002)$$
$$+ 3/7(g_\perp - 2.002) + 0.04$$

For covalent bonding, α^2Cu is between 0.75 and 0.80, and for ionic bonding, it approaches 1. The value for these Cu(II) complex supported the covalent character of the Cu—O bond in the Cu(II) complex. The value of g_{av} of the Cu(II) complex was 2.14. For the covalent complexes, it was less than 2.3, and for ionic complexes, it is normally 2.3 or larger. Thus, the covalent nature of this complex was confirmed.

Thermogravimetric analysis

To study the thermal stability and decomposition patterns of the crosslinked polymers, dynamic thermogravimetric analysis was undertaken.[28] The thermogravimetric curves of the 4% NNMBA-crosslinked PAA, the sodium salt, and its Cu(II) complex were recorded in air.

In NNMBA–PAA, the first-stage decomposition occurred from 33 to 305°C with a weight loss of 29%. This was due to the evolution of adsorbed and coordinated water molecules. The second-stage decomposition occurred from 305–440°C with a weight loss of 42%. This might have been due to the rupture of crosslinking and the breaking of polymeric linkages. From 440°C onward, the whole substance was converted to easily vaporizable gases with a weight loss of 29%.
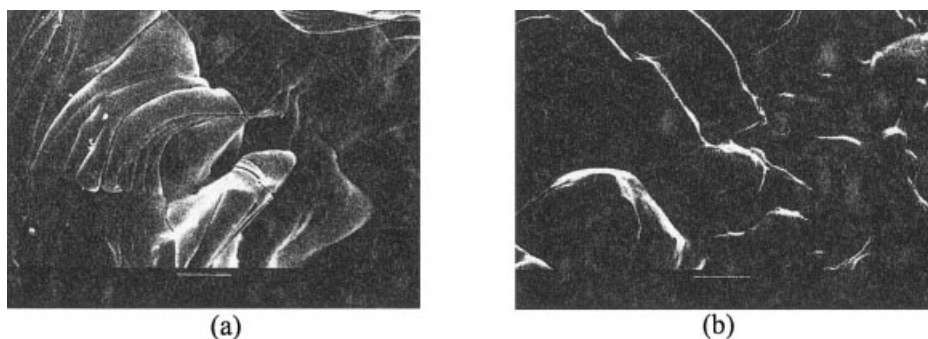

Figure 6 Scanning electron micrographs of 4 mol % NNMBA-crosslinked (a) PAA and (b) Cu(II) complex.
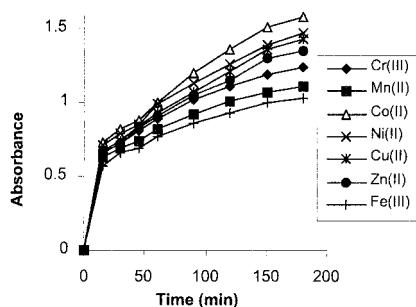
Figure 7 Catalytic activity of the various metal complexes of the sodium salt of 4 mol % NNMBA-crosslinked PAAs.

In the case of the sodium salt resin, the first-stage decomposition occurred from 46 to 350.73°C with total weight loss of 34% because of the evolution of adsorbed and coordinated water molecules. The second-stage decomposition from 350 to 363°C occurred with a weight loss of about 42% because of the rupture of polymeric linkages and crosslinkings. The third-stage decomposition with a weight loss of about 8% occurred from 363 to 457°C because of the evolution of CO_2 and other vaporizable gases. About 11.25% NaO remained at 677°C.

Because the water uptake capacity of the Cu complex was lower, the first-stage decomposition occurred from 35 to 241°C with a weight loss of about 14%. This was due to the evolution of adsorbed and coordinated water. The second-stage decomposition occurred from 241 to 319°C with a weight loss of about 13%. This might have been due to the rupture of polymer–copper coordinate bonds. As a continuation of this, the rupture of crosslinking and polymeric linkages occurred with a weight loss of 16% from 319 to 361°C. From 361 to 454°C, the whole polymeric moiety might have transferred to gases such as CO_2 and H_2O. After that, the weight of the residue, that is, cupric oxide, remained constant.

SEM

SEM is the most widely used technique to study the shape, size, morphology, and porosity of polymers. The change in the surface morphology of the polymeric ligand with complexation was investigated with this technique.

In this study, SEM was used to probe the change in morphological features of the NNMBA-crosslinked polymeric ligand on complexation. PAA with 4 mol % crosslinked NNMBA and its Cu(II) complex were investigated with the SEM technique. The SEM pictures of 4 mol % NNMBA-crosslinked PAA and its copper complex are given in Figure 6. The SEM of the uncomplexed resin had a smooth surface. The voids/channels present in the crosslinked polymer matrix were responsible for the swelling of the polymer and the

reactivity of the active sites buried within the three-dimensional crosslinked polymer matrix. The voids disappeared on complexation because of the contraction of the polymer matrix. The surface became rough, resulting from the rearrangement of the already ordered macromolecular chains for complexation.

Catalytic activity of the metal complexes of the sodium salt of 4 mol % NNMBA-crosslinked PAA

To investigate the catalytic activity of 4% NNMBA-crosslinked PAA–metal complexes, the hydrolysis of p-nitrophenyl acetate was chosen as a model reaction. The catalytic activity of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes of 4% NNMBA-crosslinked PAA was compared to the hydrolysis of p-nitrophenyl acetate in the absence of metal complexes. The catalytic activity decreased in the order Co(II) > Ni(II) > Cu(II) ≈ Zn(II) > Cr(III) > Mn(II) > Fe(III).

Transition metals with their variable valency and unpaired electrons in the d orbital may form unstable intermediate compounds and, hence, enhance the reaction. This was the reason the Co(II) complex exhibited the maximum catalytic activity. Mn(II) and Fe(III) showed less activity compared to Co(II) because of the presence of half-filled d orbitals. Complexes where the metal is in the +III oxidation state are generally more stable than those where the metal is in the +II state. Hence, Fe(III) and Cr(III) had a lower tendency to form intermediate complexes compared to Ni(II) and Co(II). The variation in the reactivity of the various metal complexes of sodium salt of 4% NNMBA-crosslinked PAA is shown in Figure 7.

Kinetics of the hydrolysis of p-nitrophenyl acetate catalyzed by the Co(II) complex of 4 mol % NNMBA-crosslinked PAA

In this study, kinetic studies of hydrolysis of p-nitrophenyl acetate were followed by the Co(II) complex of 4 mol % NNMBA-crosslinked PAA at three different temperatures (20, 29, and 38°C). The hydrolysis was
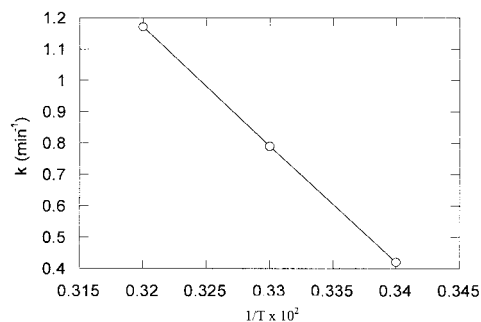

Figure 8 Variation of the rate constant with temperature in the hydrolysis of NPA catalyzed by the Co(II) complex of the sodium salt of 4 mol % NNMBA-crosslinked PAA.
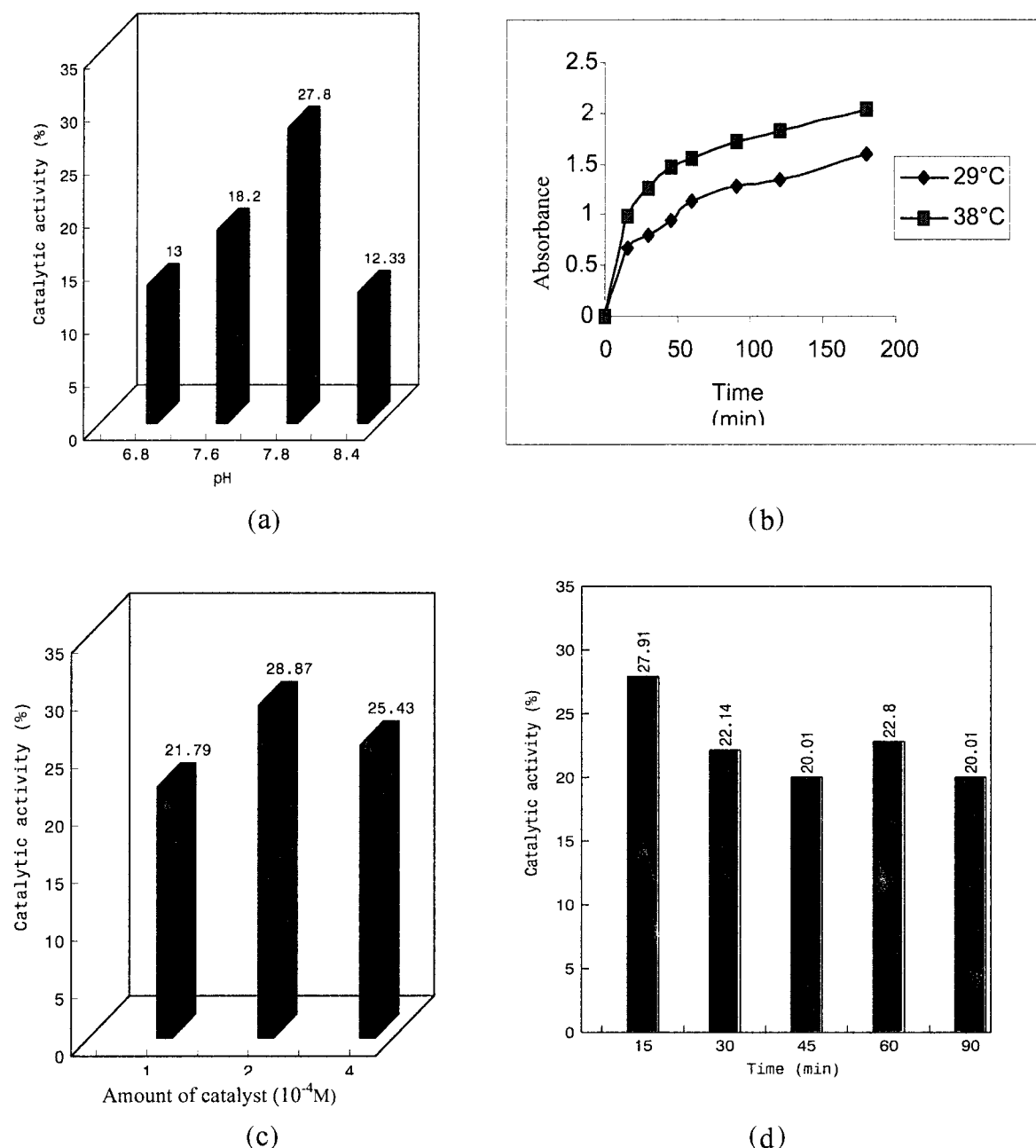
(a)

(b)

(c)

(d)

Figure 9 Effects of various parameters on the hydrolysis of p-nitrophenyl acetate catalyzed by the Co(II) complex of the sodium salt of 4 mol % NNMBA-crosslinked PAA: (a) pH, (b) temperature, (c) amount of the catalyst, and (d) time.

first order. The variation of rate constants with temperature is given in Figure 8. Compared to other metal complexes, the Co(II) complex was very active because it required a lower activation energy. The kinetic parameters for the Co(II) complex catalyzed hydrolysis were calculated with the Arrhenius equation $k = Ae^{-E/RT}$. The kinetic parameters were $E = 29.7$ kJ; $A = 1.08 \times 10^5$ s^{-1}; $\Delta S = -148.69$ J

The lower activation energy of the Co(II) complex was caused by the unsaturation in the coordination sphere, giving the p-nitrophenyl acetate molecule easy accessibility to get involved in the catalytic hydrolysis.

Effect of various parameters on the hydrolysis of p-nitrophenyl acetate

The effect of various parameters such as time, temperature, amount of catalyst, pH, and concentration of buffer had vital role in the hydrolysis of p-nitrophenyl acetate. The Co(II) complex of 4 mol % NNMBA-crosslinked PAA was used for these investigations, and the results are depicted in Figure 9. A heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes

reaction. Often this modification takes the form of a fragmentation of the reactant molecules. The activity of a catalyst depends on the strength of chemisorption. To be active, the catalyst should be extensively covered by adsorbate, which is the case if chemisorption is strong. If the strength of the substrate–adsorbate bond becomes too great, the activity declines either because the other reactant molecules cannot react with the adsorbate or because the adsorbate molecules are immobilized on the surface. This pattern of behavior suggests that the reactivity of a catalyst should initially increase and then decrease. This is the reason why the rate of catalysis was not uniform with time. This suggests an acetylation–deacetylation mechanism for the catalytic activity of the polymer–metal complexes in ester hydrolysis. The catalysis started with the adsorption of the acetyl group, which took place at a higher rate initially. As adsorption increased, the rate of catalysis also increased to some extent and then decreased.

The influence of pH was studied with phosphate buffer with pH values 6.8, 7.6, 7.8, and 8.4 and was on the order 6.8 < 7.6 < 7.8 > 8.4. The absorbance at 400 nm was observed only after 45 min at pH 6.8 because the rate of hydrolysis of p-nitrophenyl acetate at pH 6.8 is very low. Although the rate of hydrolysis increased with increase in pH, the maximum catalytic activity was observed at pH 7.8 and then decreased. The decrease in catalytic activity at pH 8.4 was due to the decreased availability of the active site of the metal complex for ester hydrolysis by the interference of the buffer ions. From this, we concluded that the acid hydrolysis of p-nitrophenyl acetate was not catalyzed by the Co(II) complex of PAA, and the optimum pH was 7.8. Buffers of concentrations ranging from 0.025 to $0.1M$ were used, and the catalytic activity was at a maximum at a concentration of $0.05M$. The catalytic activities of the Co(II) complex of 4 mol % NNMBA-crosslinked PAA at room temperature and 38°C were compared, and we found that as temperature increased, catalytic activity also increased. This complex could be used several times without loss of efficiency.

CONCLUSIONS

The preceding investigations on the metal complexation behavior of the sodium salt of 4 mol % NNMBA-crosslinked PAA revealed that the complexation behavior was significantly influenced by the microenvironment around the ligand functions. The metal-ion uptake of this polymer decreased in the order Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II). The polymeric ligand was characterized by ^{13}C-NMR CP-MAS spectroscopy. The IR characteristics of the ligand group were used for tracing the complexation with metal ions. The presence of metal ion lowered the stretching frequencies of the ligand. The UV–vis absorption studies indicated the geometry and structure of different metal complexes. EPR parameters of the polymer-anchored Cu(II) complexes provided a definite clue about the nature of the ligand–metal bond. SEM revealed the change in the surface morphology of the polymer on metal-ion complexation. The swelling characteristics were measured as EWC to follow the swelling ability of the studied system in water. Thermal studies were also carried out. The effect of the metallated resins on the rate of hydrolysis of p-nitrophenyl acetate was studied. No catalytic effect was observed for ester hydrolysis by mineral acid, whereas alkaline hydrolysis had a marked influence. The variation in reactivity with metal ions could be explained in terms of their coordination geometry. The Co(II) complexes exhibited high catalytic activity compared with other metal complexes. The rate of catalysis was influenced by conditions such as time, temperature, solvent, and pH.

References

1. Iseid, S. S.; Kuchn, G.; Lyon, J. M.; Merrifield, R. B. J Am Chem Soc 1982, 104, 2632.
2. Calman, G. J Am Water Assoc 1981, 73, 652.
3. Bolto, B. A. J Macromol Sci Chem 1980, 14, 107.
4. Sasaki, Y.; Walter, L. L.; Hurst, E. L.; Pittmann, C. D., Jr. J Polym Sci Polym Chem Ed 1975, 11, 1313.
5. Leadbeater, N. E.; Marco, M. Chem Rev 2002, 102, 3217.
6. Patel, S.; Sinha, S.; Mishra, A. N.; Kamath, B. V. J Mol Catal A 2003, 192, 53.
7. Cruetz, C.; Sutin, N. Proc Natl Acad Sci USA 1975, 72, 2858.
8. Gubitosa, G.; Brintzinger, H. H. J Organomet Chem 1977, 140, 187.
9. Nakamura, Y.; Hirani, H. Chem Lett 1976, 1197.
10. Geoff, K.; Simon, J. H.; Nikki, P. Analyst 1992, 117, 1243.
11. Kuhn, W.; Kamel, A.; Walten, D. H. Chimia (Zurich) 1958, 12, 123.
12. Lingen, J.; Yan, J. React Polym 1992, 1, 54.
13. Lindsay, D.; Sherrington, D. C.; Greig, J. A.; Hancock, R. D. React Polym 1990, 12, 75.
14. Xinggin, L.; Zhixing, S.; Wengun, Z.; Guangyao, Z.; Xijan, F. J Anal Chem 1992, 344, 2525.
15. Kumar, G. S. V.; Mathew, B. Eur Polym J 1998, 34, 1185.
16. Bamaszal, L.; Watson, J. C.; Kendrew, J. C. J Mol Biol 1965, 12, 130.
17. Geckeler, K. E. Pure Appl Chem 2001, 73, 129.
18. Kasgoz, H. Polymer 2001, 42, 7497.
19. Silverstein, R. M.; Bassler, G.; Morill, T. C. Spectrometric Identification of Organic Compounds, 4th ed.; Wiley: New York, 1981.
20. Vogel, A. I. A Text Book of Quantitative Inorganic Analysis; Longman: London, 1978.
21. Seidl, J.; Stumbery, J. Chem Ind 1960, 190.
22. Mayers, E. M.; Fritz, J. S. Angew Chem 1977, 49, 418.
23. Yamada, M.; Takagi, M.; Ueno, K. J Coord Chem 1980, 10, 257.
24. Janes, L.; Morcellet, J.; Delperte, M. M. Eur Polym J 1992, 28, 185.
25. Lieser, K. H.; Kurbouy, M.; Thubusch, B. Angew Makromol Chem 1987, 152, 69.
26. Egawa, H.; Honaka, T. J. J Appl Polym Sci 1986, 311, 677.
27. Kalalova, E.; Radova, Z.; Svee, F.; Kalal, J. Eur Polym 1977, 13, 293.
28. Wendlandt, W. W. Thermal Methods of Analysis; Interscience: New York, 1964.
29. Kivelson, J. D.; Neiman, R. J Chem Phys 1961, 35, 149.